

*The Absorption Spectra of the Vapours of Benzene and its Homologues at Different Temperatures and Pressures, and likewise of Solutions of Benzene.*

By WALTER NOEL HARTLEY, F.R.S., D.Sc., Royal College of Science, Dublin.

(Received August 15,—Read December 12, 1907.)

(Abstract.)

The author having been engaged since the year 1877 in investigating and correlating the physical and chemical properties of aromatic substances in relation to their chemical structure or constitution, he has latterly found it desirable that several very definite compounds should be examined in a state of vapour, as well as in solution.

The work of E. Pauer,\* W. Friederichs,† and of L. Grebe‡ is referred to in detail. The vapours of benzene and several of its derivatives have been examined (1) at different temperatures and constant pressure; and (2) at different pressures, the temperature being constant. The previous measurements of Pauer, Friederichs, and Grebe have been confirmed, and reconciled where they do not show complete agreement with each other. The records of temperature and pressure, and the shortening of the exposure of the photographic plates, constitute important differences between the work of the former investigators and that of the author.

Details of the following photographs are given :—

Absorption Bands in the Spectrum of Benzene Vapour at Different Temperatures and a Barometric Pressure of 755·5 mm.

Temperatures .....	12°·5	25°	43°	53°
Number of bands photographed and measured	55	84	82	56

Absorption Bands in the Spectrum of Benzene Vapour at 11°·5 and Different Pressures.

Pressures in millimetres .....	778	483	253	21
Number of bands measured .....	36	38	46	44

The same at 100° and Different Pressures.

Pressures in millimetres .....	683	589	478	381	279	172
Number of bands measured .....	9	13	14	16	17	18

The same at 100°.

Pressures in millimetres .....	767	591	484	332	206	142	99	88
Number of bands measured .....	5	9	9	12	13	11	14	15

The same at 100°.

Pressures in millimetres .....	92	69	43
Number of bands measured .....	25	36	50

\* 'Annalen,' 1897, vol. 61, p. 363.

† 'Zeitschr. f. Wissenschaftliche Photographie,' 1905, p. 633.

‡ *Loc. cit.*, 1905, p. 363.

The same at 100°.

Pressures in millimetres.....	67·5	52·5	37·5	28·5	22·5	15·5	9	5	4
Number of bands measured	31	54	60	72	75	88	52	38	30

Absorption Bands in the Spectrum of Toluene Vapour at Different Temperatures and Constant Pressure.

Temperatures.....	10°	30°	40°	50°	60°	70°	80°	90°	100°
Number of bands measured	16	20	16	20	23	21	24	23	18

The Absorption Spectrum of Toluene Vapour at Different Pressures and Constant Temperature.

Pressures in millimetres.....	763	563	371	174	43
Number of bands measured .....	18	16	18	15	15

The Absorption Bands of Ethylbenzene Vapour at Different Temperatures.

Temperatures.....	16°·5	40°	70°	100°
Number of bands measured...	19	18	8	2

General absorption  
occurs here.

The same.

Temperatures.....	20°	36°	52°	71°	100°
Number of bands measured...	17	15	5	3	Complete absorption..

The Absorption Bands of *o*-Xylene Vapour at Different Temperatures.

Temperatures .....	20°	45°	72°	100°	121°
Number of bands measured.....	23	21		No bands, general absorption.	

Absorption Bands of *m*-Xylene Vapour at Different Temperatures.

Temperatures .....	11°	40°	70°	100°
Number of bands measured.....	26	41	6	5

General absorption occurs  
between 2652 and 2429.

The same, *p*-Xylene Vapour.

Temperatures.....	10°	40°	70°	100°
Number of bands measured	30	25	5	7

General absorption from  
2790 to 2416.

The same, Cymene Vapour.

Temperatures.....	17°·5	40°	70°	100°
Number of bands measured	0	7	9	9

The same, Mesitylene Vapour.

Temperatures .....	18°·5	45°	72°	100°	120°	140°
Number of bands measured	2	2	2	2	General absorption,	

The measurements are given of similar groups of bands which occur in the vapour-spectra of benzene, toluene, ethyl benzene, and the three isomeric xylenes; benzene and toluene being compared at ordinary temperatures and also at 30° below their respective boiling points. A tabulated statement is also made of the heads of strong bands which appear to be common to benzene and its homologues. The intensities of the bands in the benzene vapour-spectrum at 100°, and different pressures, were compared with those at temperatures below its boiling point, and it was seen that the bands at

100° are almost identical with those at lower temperatures, but with this difference, that, at lower temperatures, some of the bands at the less refrangible end of the spectrum are feeble and less well defined. The vapour-spectrum of benzene is divided into groups of bands which are caused by the overlapping of two or more similarly constituted spectra differing in intensity. The strong bands number 54, there being 27 in each of two spectra. In addition, there are 30 feeble bands, which also fall into two series of similar groupings, but with less regularity. The entire number of bands observed between 12°·7 and 25°, under a pressure of 759·5 mm., are thus resolved into four spectra, of which two are composed of strong and two of weak bands.

#### *Summary and Conclusions.*

As regards the vapour-spectra, it is proved that benzene at 100° C. has the same molecular mass as at 25° or 12°·7.

The absorption bands at 100° are almost identical with those at lower temperatures, with variations as to definition in the less refrangible rays. The important influence of the position of the substituted hydrogens in benzene, upon the number and position of the bands in the spectra of its homologues, is clearly demonstrated.

Variations in the spectra of benzene at different temperatures and pressures are explained by the fact that there are two different kinds of absorption which are sharply defined and may be differentiated. First, there is the general absorption, which is broadened and extended towards the less refrangible rays by rise of temperature; secondly, there is the selective absorption, which includes all the narrow individual bands and groups of bands; they are not widened and displaced by rise of temperature, and such changes of this nature that they undergo are the effect of the overlying general absorption. The selective absorption is best studied by raising the general absorption to a maximum (at 100°), and studying the spectra produced by reduction of pressure. In this manner, any changes due to general absorption are eliminated. From the fact that increased sharpness and definition of the narrow bands is easily produced by rise of temperature, and also by reduction of pressure, the general absorption is clearly shown to be caused by encounters between the molecules, and the numerous narrow bands are to be ascribed to the vibrations of the atoms or atom-complexes within the molecules. This confirms the conclusion drawn from the study of solution-spectra published in 1881,\* in 1882,† and 1885.‡

\* 'J. Chem. Soc.', vol. 39, pp. 153—165.

† *Loc. cit.*, vol. 47, pp. 685—757.

‡ 'Phil. Mag.', 1885, vol. 19, 5th ser., p. 35.

The similar groups of bands occurring in benzene and toluene, and the close similarity between the spectra of toluene and ethylbenzene, with the further resemblance between *m*-xylene and toluene and ethylbenzene, is evidence that the mode of vibration within the benzene nucleus or ring-structure is in a great measure unaffected by the side-chain substitution.

A distinction is drawn between the absorption spectra of vapours, called *vapour-spectra*, and of solutions, called *solution-spectra*, and the relationship of one to the other is explained. Previous investigations carried on by the author for many years are briefly referred to, and it is shown how the views entertained have been confirmed by the investigation of the *vapour-spectra*. Attention is drawn to the insufficiency of ordinary chemical formulæ to represent the constitution of organic compounds, particularly of those like benzene which are of an endothermic character, since they do not take into account the distribution of energy in the molecule, and this obscures the view of the physical character of chemical structure or constitution. In short, whereas bonds and linkings in the formulæ usually written belong to a conception of chemical structure which is statical, the molecular constitution of such substances as are under discussion, when based upon the evidence derived from their optical properties, is essentially dynamical.\* The relation of *solution-spectra* to *vapour-spectra* is shown, by reference to the results obtained by Pauer, Hartley and Dobbie, and by Grebe. The view entertained by Baly and Collier† that benzene has seven and no more than seven *solution-bands*, indicative of a definite making and breaking of a double linkage of the carbon atoms in the ring, has been carefully examined, and the author finds this to be incompatible with well-ascertained facts. From the measurements and numerical relations of the wave-lengths of bands in *solution-* and *vapour- spectra* it is explained how four, six, seven, eight, or nine bands may be recognised in *solution-spectra*, six of which are similarly constituted, and four of these are not only similarly constituted but very nearly of equal width, intensity, and persistency, that is to say, they have the same coefficient of extinction, and in all other respects an almost exact similarity. They correspond with four groups of *vapour-bands* which are formed by the four different series of bands which overlap, and they occur where they overlap to the greatest extent.

\* "Single, double, or treble linkings are simply an incomplete method of representing the relation of the carbon-atoms to each other at some particular phase of their vibrations" ("Phil. Mag.", 1885, vol. 19, pp. 55-57).

† "Chem. Soc. Trans.", 1905, vol. 87, p. 1332.